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Four new isoflavanones from *Tadehagi triquetrum*

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Abstract: Four new isoflavanones with isoprenoid units, named triquetrumones E–H (**1**–**4**), were isolated from the whole plants of *Tadehagi triquetrum*. The structures were elucidated on the basis of spectroscopic analyses, including application of MS, UV, IR, 1D and 2D NMR spectroscopic techniques.

Keywords: Tadehagi triquetrum, isoflavanone, triquetrumone

Introduction

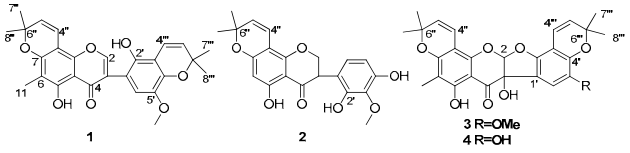
Tadehagi triquetrum (Linn.), belonging to the family of Papilionaceae, is an endemic shrub widely distributed in the southern area of Yunnan Province, China. As a traditional DAI medicine in southwest of China, it has been widely used for the treatments of anthelminthic, stomachic, antimicrobial, and inflammation. In addition, it also has been used as a nutrientand appetitive feedstuff.[1,2]

Previous phytochemical studies found a few of isoflavones and phenols from this species.[3,4] As a part of our continuing research on medicinal plants of DAI ethnopharmacy,[6–10] we investigated the chemical constituents of the whole plants of *T. triquetrum*, which led to the isolation of four new isoflavanones, named triquetrumones E–H (**1**–**4**). Isoflavanones possessing isoprenoid unit, can be considered as the characteristic constituents in this plant. This paper describes the isolation and the structural elucidation of these four new compounds.

Results and Discussion

Compound **1** was obtained as yellow amorphous powder which showed an orange fluorescence under UV at 365 nm. The molecular formula was determined as $C_{27}H_{26}O_7$ by HRFABMS ($[M + H]^+$ at *m/z* 463.1738). The IR spectrum showed bands at 3440 (OH), 1637 (C=O), and 1604 (aromatic ring) cm^{-1}. In the ^1H NMR spectrum (Table 1), one singlet at δ_H 8.03 (s, H-2), an aromatic C-methyl group at δ_H 2.12 (s, H-11), two phenolic hydroxyl at δ_H 12.62 (br. s) and 8.05 (br. s), one methoxyl group at δ_H 3.84 (s) and two 2,2-dimethylpyran rings at δ_H 5.62 (d, *J* = 9.9, H-5"), 6.71 (d, *J* = 9.9, H-4"), 1.48 (s, H-7",8") and 5.63 (d, *J* = 9.9, H-5'"), 6.82 (d, *J* = 9.9, H-4'"), 1.50 (s, Me-7'" and Me-8'") were observed. In addition, the ^{13}C NMR spectrum (Table 2) displayed 15 skeletal C atoms: one carbonyl at δ_C 181.9, 13 quaternary C-atoms at δ_C 104.7–159.1, and as well one CH group at δ_C 154.7. Considering the above NMR data and the orange fluorescence under UV at 365nm, the structure was proposed to be an isoflavone, possessing two isoprenoids units.[3]

The HMBC correlations (Fig. 1) of H-5"/C-8 and H-4" with C-6", C-7, and C-9, and of H-5'"/C-3', and H-4'" with C-6'" and C-4' suggested that two dimethylpyrano rings were condensed to C-7/8 and C-4'/3', respectively. A methyl at δ_H 2.12 was assigned to connection with C-6 by its correlations with C-5, 6, 7 in the HMBC spectrum. Moreover, two OH groups were placed at C-5 and C-2', respectively, and a methoxyl group was positioned at C-5' by HMBC experiments. Complete analysis of the ^1H and ^{13}C NMR, HSQC, HMBC data established the structure of **1** as (5,2'-dihydroxy-5'-methoxyl-6-methyl[6",6"-dimethylpyrano-(2",3":7,8)]-[6'",6'"-dimethyl-pyrano(2'",3'":4',3')]-isoflavanone, and named triquetrumone E.



Compound **2** was isolated as yellow amorphous powder. It gave a molecular formula $C_{21}H_{20}O_7$ by HRFABMS ($[M + H]^+$ at *m/z* 385.1274). Bands for OH and carbonyl functional groups were assumed by IR absorption at 3421 and 1647 and UV absorptions at 270 nm were typical for an isoflavanone.[11] The NMR spectra of compound **2** (Tables 1 and 2) were similar to those of 1'",2'"-dehydrocyclokievitone,[12] except for the appearance of a methyoxyl group (δ_H 3.78, δ_C 60.7) in **2**, which was also supported by its molecular formula. The

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Table 1. ^{1}H NMR data of 1–4.

position	1[a]	2[b]	3[c]	4[b]
2	8.03, s	4.53, dd (5.5, 10.9); 4.64, t (10.9)	6.32, s	6.29, s
3		4.27, dd (10.8, 5.5)		
6		5.88, s		
11	2.12, s		1.92, s	1.92, s
5'		6.38, d (8.4)		
6'	6.57 , s	6.69, d (8.4)	6.89, s	6.78, s
4"	6.71, d (9.9)	6.51, d (10.1)	6.46, d (9.9)	6.57, d (10.0)
5"	5.62, d (9.9)	5.60, d (10.1)	5.77, d (9.9)	5.67, d (10.0)
7"	1.48, s	1.41, s	1.38, s	1.38, s
8"	1.48, s	1.42, s	1.42, s	1.41, s
4"'	6.82, d (9.9)		6.57, d (10.0)	6.46, d (9.9)
5"'	5.63, d (9.9)		5.68, d (10.0)	5.76, d (9.9)
7"'	1.50, s		1.41, s	1.38, s
8"'	1.50, s		1.45, s	1.41, s
OMe	3.84, s	3.78, s	3.73, s	
OH(5)	12.62, br. s	12.44, br. s	12.27, br. s	12.27, br. s
OH(2')	8.05, br. s	8.15, br. s		
OH(4')		8.30, br. s		
OH(5')				7.50, br. s
OH(3)			6.08, br. s	6.05, br. s

[a]Measured in $CDCl_3$ at 400MHz; [b]Measured in acetone-d_6 at 500MHz; [c]Measured in acetone-d_6 at 400MHz.

methyoxyl group was paced at C-3', supported by the HMBC correlations (Fig. 1). Thus, compound **2** was established to be 5,2',4'-trihydroxy-3'-methoxy[6",6"-dimethylpyrano(2",3":7,8)]-isoflavavone, and named triquetrumone F.

Compound **3** appeared as yellow amorphous powder whose molecular was established as $C_{27}H_{26}O_8$ by HRFABMS at *m/z* 479.1723 (calcd. for $C_{27}H_{27}O_8$, 479.1706), which indicated 15 degrees of unsaturation. *T. triquetrum* are known to contain three 5-hydroxy-coumaronochromones, and all of which fluoresce on silica gel thin-layer plates under 365 nm of UV light.[3] Take UV, MS, and NMR data into account, compound **3** can be most logically formulated as an isoflavone, in which C-2 and C-2' was linked by an ether oxygen to form a pentacyclic ring system.[13] The ^{1}H NMR spectrum (Table 1) of **3** revealed two 2,2-dimethylpyrane rings at δ_H 5.77 (d, J = 9.9, H-5"), 6.46 (d, J = 9.9, H-4"), 1.38 (s, Me-7") and 1.42 (s, Me-8"), together with 5.68 (d, J = 10.0, H-5"'), 6.57 (d, J = 10.0, H-4"'), 1.41 (s, Me-7"') and 1.45 (s, Me-8"'), associated with an aromatic C-methyl group at δ_H1.92 (s) and two singlets at δ_H 6.32 (s, H-2) and 6.89 (s, H-6'), respectively.

The ^{13}C and ^{1}H NMR spectra of **3** implied that this compound might be an analogue of triquetrumone B.[3] Careful comparison of the NMR data of two compounds revealed that one more OH group might be appeared at C-3, suggested by downshift signals at δ_C 79.4 (s, C-3), δ_H 6.08 (br. s, OH) in **3**. The proposal was further supported by the HMBC correlations (Fig. 1) between OH-3 with δ_C 193.4 (s, C-4), 111.5 (d, C-2) and 79.4 (s, C-3). Thus, **3** was established as 3,5-dihydroxy-5'-methoxyl-6-methyl[6",6"-dimethylpyrano(2",3":7,8)]-[6"',6"'-dimethylpyrano(2"',3"':2',3')]coumaronochromone, and named triquetrumone G.

Compound **4** was obtained as yellow amorphous powder. The HRFABMS clearly showed the $[M + H]^+$ in agreement with the molecular formula $C_{26}H_{24}O_8$. The UV, IR, and NMR spectroscopic data also suggested a coumaronochromone structure for **4**,[14] which was very similar to those of **3**. Detailed comparison of the NMR data of two compounds revealed that a hydroxyl group was appeared on ring C of **4**, instead of the methyoxyl in **3**, concurring with its molecular formula. The assignment was also supported by the HMBC correlations (Fig. 1) of δ_H 7.50 (*s*, OH-5') with δ_C 106.9 (s, C-3'), 142.1 (s, C-4') and 143.0 (s, C-5'). Thus, the structure of **4** was established as 3,5,5'-trihydroxy-6-methyl[6",6"-dimethylpyrano(2",3":7,8)]-[6"',6"'-dimethypyrano(2"',3"':2',3')]coumaronochromone, and named triquetrumone H.

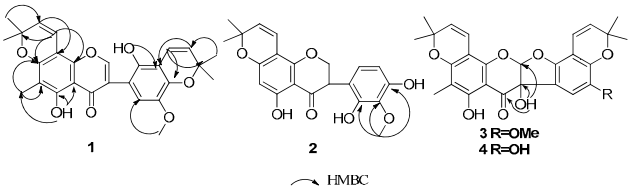

Fig 1. Key HMBC correlations of **1**–**4**.

Experimental Section

General Experimental Procedures. Column chromatography (CC): Silica gel (200–300 mesh, *Qingdao Marine Chemical corporation*, China) and Sephadex LH-20 (*Amersham Biosciences,* Sweden); TLC monitoring, visualization by heating the silica gel plates sprayed with 10% H_2SO_4 in EtOH. Optical rotations: *Horiba SEPA-300* polarimeter. UV spectra: *Shimadzu 210-A* double-beam spectrophotometer; λ_{max} (logε) in nm. IR Spectra: *Brucker Tensor 27* spectrometer ; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker AM-500* spectrometers; δ in ppm with $SiMe_4$ as internal standard, J in Hz. MS: *VG Autospec-3000* and *API QSTAR-Palsar-I* spectrometer.

Plant Material. The whole plants of *Tadehagi triquetrum* were collected from Xishuangbanna, Yunnan Province, China, in April 2007. Its identity was confirmed by Mr. Jing-Yun Cui, and a voucher specimen (NO. 2007042) has been deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The dried and milled sample (10 kg) were soaked in 95 % EtOH (40 L × 3) under reflux (48 h × 3), and the solvent was evaporated *in vacuo*. The

Table 2. ^{13}C NMR data of 1–4.

pos.	1[a]	2[b]	3[c]	4[b]
2	154.7, CH	71.2, CH_2	111.5, CH	111.4, CH
3	123.4, C	47.5, CH	79.4, C	79.3, C
4	181.9, C	198.5, C	193.4, C	193.6, C
5	159.1, C	165.0, C	162.4, C	162.3, C
6	109.8, C	97.6, CH	107.0, C	107.1, C
7	158.3, C	162.4, C	161.4, C	161.3, C
8	100.5, C	102.3, C	102.6, C	102.5, C
9	150.1, C	158.2, C	152.1, C	152.7, C
10	104.7, C	103.9, C	100.7, C	101.6, C
11	7.3, C		6.8, CH_3	6.8, C
1'	110.8, C	114.0, C	117.5, C	118.2, C
2'	146.1, C	149.6, C	150.3, C	148.8, C
3'	113.6, C	136.4, C	107.6, C	106.9, C
4'	144.5, C	150.9, C	145.4, C	142.1, C
5'	142.8, C	108.3, CH	146.0, C	143.0, C
6'	114.1, CH	125.7, CH	110.6, CH	111.7, CH
4"	114.6, CH	116.0, CH	115.8, CH	115.8, CH
5"	129.4, CH	127.3, CH	128.1, CH	128.0, CH
6"	78.3, C	78.7, C	79.4, C	79.3, C
7"	28.3, CH_3	28.3, CH_3	28.0, CH_3	27.7, CH_3
8"	28.3, CH_3	28.5, CH_3	28.7, CH_3	27.8, CH_3
4"'	117.8, CH		116.3, CH	116.3, CH
5"'	127.5, CH		131.6, CH	131.7, CH
6"'	76.5, CH		77.6, C	77.8, C
7"'	27.8, CH_3		28.6, CH_3	28.5, CH_3
8"'	27.8, CH_3		29.3, CH_3	28.6, CH_3
OMe	57.4, CH_3	60.7, CH_3	57.5, CH_3	

[a]Recorded in $CDCl_3$ at 100MHz; [b]Recorded in acetone-d_6 at 100MHz; [c]Recorded in acetone-d_6 at 125 MHz.

residue was partitioned between EtOAc and H_2O. The EtOAc extract (80 g) was subjected to CC ($CHCl_3$/Me_2CO 10:1→1:1): eight fractions (*Fr.1–8*) by TLC. *Fr.3* (15 g) was repeatedly subjected to CC (1. Silica-G petroleum ether/Me_2CO 10:1→2:1; 2. *Sephadex* LH-20, $CHCl_3$/MeOH 1:1) to afford **1** (6 mg). *Fr.4* (12 g) was purified by repeated CC (SiO_2, petrolrum ether/Me_2CO 3:1) to afford **2** (21 mg). *Fr.5* (10 g) was resubmitted to CC (1. SiO_2, $CHCl_3$/MeOH 70:1→50:1; 2. *Sephadex* LH-20, MeOH/H_2O 9:1) to provide **3** (5 mg) and **4** (25 mg).

Triquetrumone E (1): yellow amorphous powder, UV (MeOH) λ_{max} (log ε) 273 (4.49), 212 (4.51) nm. IR (KBr) ν_{max} 3440, 2924, 1637, 1604 cm^{-1}. ^{1}H and ^{13}C NMR data see Tables 1 and 2. ESIMS (positive): 463 ([M + H]$^+$). HRFABMS (positive): 463.1738 ([M + H]$^+$, $C_{27}H_{27}O_7$, calcd. 463.1757).

Triquetrumone F (2): yellow amorphous powder, $[\alpha]_D^{20}$ −1.63 (*c* 0.002, Me_2CO). UV (MeOH) λ_{max} (log ε) 270 (4.24), 207 (4.42) nm. IR (KBr) ν_{max} 3421, 1647, 1598 cm^{-1}. ^{1}H and ^{13}C NMR data see Tables 1 and 2. ESIMS (positive): 385 ([M + H]$^+$). HRFABMS (positive): 385.1274 ([M + H]$^+$, $C_{21}H_{21}O_7$, calcd. 385.1287).

Triquetrumone G (3): yellow amorphous powder, $[\alpha]_D^{20}$ −44.5 (*c* 0.001, Me_2CO). UV(MeOH) λ_{max} (log ε) 273 (4.01), 268 (4.02), 212 (4.39) nm. IR (KBr) ν_{max} 3441, 1632, 1600 cm^{-1}. ^{1}H and ^{13}C-NMR data see Tables 1 and 2. EIMS: 478 [M]$^+$. HRFABMS (positive): 479.1723 ([M + H]$^+$, $C_{27}H_{27}O_8$, calcd. 479.1706).

Triquetrumone H (4): yellow amorphous powder, $[\alpha]_D^{20}$ −32.3 (*c* 0.001, Me_2CO). UV (MeOH) λ_{max} (log ε) 274 (4.34), 268 (4.34), 212 (4.45) nm. IR (KBr) ν_{max} 3424, 1635, 1599 cm^{-1}. ^{1}H and ^{13}C NMR data see Tables 1 and 2. EIMS: 464 [M]$^+$. HRFABMS (positive): 465.1556 ([M + H]$^+$, $C_{26}H_{25}O_8$, calcd. 465.1549).

Electronic Supplementary Material

Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s13659-011-0033-5 and is accessible for authorized users.

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